Thermochemistry of Gaseous Ethylsilanes and Their Radical Cations

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The dissociation behavior of energy-selected tetraethylsilane, triethylsilane, and diethylsilane photocations is studied using the threshold photoelectron–photoion coincidence (TPEPICO) technique. In the 8–12.5 eV photon energy range, 0 K dissociation onsets have been measured from the TPEPICO data. The dissociation channels observed include loss of ethane, hydrogen molecule, ethyl radical and hydrogen atom, depending upon the molecular ion under investigation. The thermochemistry of the molecular ions and dissociation fragments is obtained by an analysis that takes into account the kinetics and internal energy distributions of the ions. The various dissociation onsets permit the reevaluation of both neutral and ionic silane thermochemistry. We observed 298-K ethyl group values of 60 ± 10 and 94 ± 10 kJ mol^{-1} for neutral and ionic silanes, respectively. These values are considerably smaller than the previously reported values of 86 and 130 kJ mol^{-1}, respectively. Finally, a $\Delta_f H°$ (298 K) of −141.5 ± 21 kJ/mol for neutral diethyl silane is derived from the dissociative ionization onset of diethylsilane. (J Am Soc Mass Spectrom 1998, 9, 597–605) © 1998 American Society for Mass Spectrometry

Photoionization mass spectrometry is an important tool in determining ion and sometimes neutral thermochemistry. However, the conversion of ionization energies and fragment ion appearance energies into ionic heats of formation is dependent upon a data base of valid heats of formation of neutral species. In the case of organic silicon compounds, this data base is far from reliable.

Recently, Lin and Dunbar [1] investigated the photodissociation kinetics of tetraethylsilane in an ICR cell. By fitting the dissociation rate constant to the statistical RRKM theory, they were able to derive a 0 K activation energy (E_0) for the ethyl loss reaction of 0.76 eV. We have also measured this reaction using threshold photoelectron photoion coincidence (TPEPICO) and obtained an onset of 0.83 eV [2]. It is highly likely that a reevaluation of the Dunbar results using a better set of vibrational frequencies will bring these two results into accordance. In the absence of a barrier for the reverse recombination reaction, the heat of formation of the triethylsilyl ion (Et_3Si^+) can be determined from the following cycle:

$$\Delta_f H°(Et_3Si^+) = \Delta_f H°(Et_4Si) + IE(Et_4Si) + E_0 - \Delta_f H°(\cdot Et) \quad (1)$$

Because the neutral heat of formation may not be reliable, it is helpful to measure this fragment ion heat of formation through other channels, such as done by Potzinger et al. [3]. For example, the triethylsilane ion also dissociates to form Et_3Si^+, by loss of H. Therefore, we have chosen to investigate tri- and diethyl silane in order to help establish a more reliable neutral and ionic thermochemistry.

Alkyl silane ions have been studied by mass spectrometry in the past [4–6]. Although most of this previous work has focused on the methyl silanes and other organosilicon compounds, a few groups have studied the ethyl silanes by mass spectrometry [4, 6–11]. No photoionization studies on the ethyl silanes have been reported.

In this work, we have measured the ionization energies (IEs) of diethyl, triethyl, and tetraethylsilane by threshold photoelectron spectroscopy. In addition, we have used the TPEPICO technique to measure the dissociation energetics and kinetics of the energy-selected ions, which we find to form fragment alkylsilicon ions with reduced silicon coordination. Ab initio methods have been used to help in characterizing the geometric and vibrational structure of these ions.

Experimental

The threshold photoelectron photoion coincidence technique has been previously described [12,13] so that only a brief summary will be included here. Ions and electrons are formed by dispersed vacuum ultraviolet radi-

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ation in an electric field of 20 V/cm. Ions of specific internal energies are selected by counting ions in delayed coincidence with threshold electrons (with initial kinetic energy less than 45 meV). This is accomplished using a combination of steradiancy analyzer [14, 15] and hemispherical electrostatic analyzer that discriminates against energetic electrons. There are, however, always some hot electrons that are transmitted through this system. This gives a total instrument function (photon+electron) with ~45-meV FWHM and a small tail extending to energies as high as 0.5 eV. This function is taken into account wherever possible in the data analysis.

Ions are then mass analyzed by time of flight (TOF) in which the electrons provide the start signal and the ions the stop signal. Ions are accelerated through two acceleration regions and pass through a 30-cm drift distance before being detected by a microchannel plate detector. If the fragment ions are formed promptly (that is, if the dissociation rate constant is greater than about 10^7 s^{-1}), the fragment ion TOF peak will be symmetric and have a width determined by the distribution of kinetic energy released in the dissociation. However, at threshold, many fragmentation reactions are slow enough (microsecond time scale) that the ions dissociate in the course of accelerating through the first region. In this case the TOF peak is asymmetric, and its shape can be used to extract a dissociation rate constant. If the rate is sufficiently slow ($k < 10^4$ s^{-1}), fragment ions cannot form prior to ion detection. As a result, the fragment ion appearance energy cannot be identified with the dissociation limit. Rather, it is simply the energy at which the dissociation rate reaches a minimum rate constant of about 10^4 s^{-1}. In these circumstances, it is necessary to model the dissociation rate constants with the statistical RRKM theory from which the true dissociation limit can be extracted. This was the procedure used to establish the dissociation limit for the ethyl loss reaction from tetraethyl silane ions [2].

In this article, we review the photoionization results for tetraethylsilane and present new data for triethylsilane and diethylsilane. The experiments were conducted with both room temperature and molecular beam cooled samples. The molecular beam data provide improved mass resolution in our time-of-flight mass spectrometry (TOF-MS) experiment. In addition, the molecular beam cooled the compounds internally to some degree prior to ionization. This provides improved energy resolution, although it is not clear if Boltzmann-like energy distributions can be expected to result from such expansions.

For tetraethylsilane, the sample bulb temperature was kept at room temperature, giving a vapor pressure of 8 torr. Adding argon as a seeding gas gave a total backing pressure of 235 torr and a seeding ratio of 3%. For triethylsilane, the sample bulb was again kept at room temperature, giving 35 torr vapor pressure. Argon was added to provide a total backing pressure of 355 torr and 10% seeding ratio. For diethylsilane, the vapor pressure at room temperature was 200 torr, so the sample was cooled to −35 °C in a slush of 1,2-dichloroethane to reduce the vapor pressure to 33 torr. Adding argon for a total backing pressure of 435 torr gave a seeding ratio of 8%.

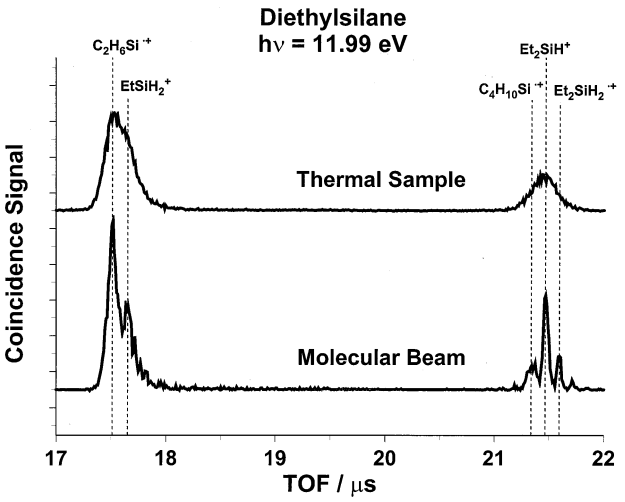

Figure 1. Diethylsilane TOF spectra obtained at a photon energy of 11.99 eV, using both thermal and molecular beam sample sources. These two spectra are normalized to equal total area. Note the improved mass resolution and higher fraction of lower-energy products Et_2SiH^+ and $C_2H_6Si^+$ in the molecular beam data.

The translational temperature can be estimated from the TOF full width at half-maximum (FWHM) and was ~8 K for all the samples used. By comparing the shift between thermal and molecular beam dissociation onsets to thermal internal energy calculations, we can estimate the effective internal temperature of the molecular beam samples, as well as the amount of internal energy removed in the expansion. Tetraethylsilane has an average internal (ro-vibrational) energy at 298 K of ~375 meV. The crossover energy shift when the thermal sample was replaced by the molecular beam sample was 267 meV. Thus, the remaining average internal energy of the molecular beam sample is ~100 meV, which corresponds to a Boltzmann temperature of 146 K. At room temperature, triethylsilane has ~283 meV of internal energy. The measured crossover shift of 186 meV implies that 97 meV remained in the molecular beam sample, which corresponds to an effective temperature of ~158 K. Diethylsilane has an average internal energy of ~194 meV at room temperature. However, because H_2 loss is one of the lowest-energy dissociation paths, we cannot measure the crossover point from the thermal data with its poor mass resolution. However, from the shift in the $C_2H_6Si^{+\cdot}$ onset, we estimate that ~120 meV of internal energy is removed by the molecular beam, leaving 74 meV (~183 K) of internal energy in the molecules.

The effect of thermal energy on the TOF mass spectrum of diethylsilane is illustrated in Figure 1. Replacing the thermal sample by a molecular beam

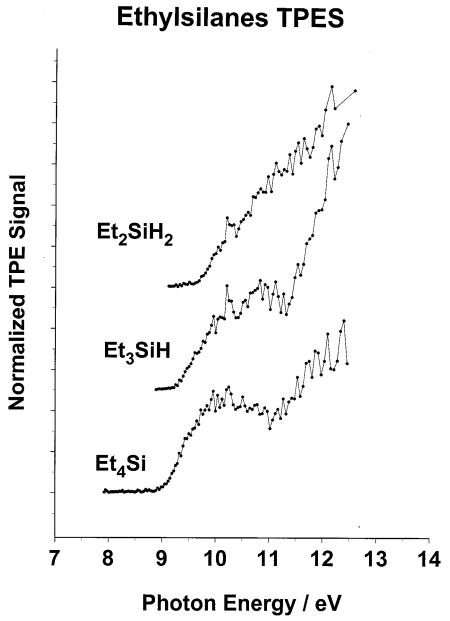

Figure 2. Threshold photoelectron spectra of the three compounds considered. The onset energies were used in the determination of adiabatic ionization energies. The broadband structure evident in these spectra can be explained by poor Franck–Condon overlap between the neutral and ion ground state geometries. This leads to a shift of ~1 eV or more between the adiabatic onset and the vertical IE (center or maximum of the first band).

improves the mass resolution and decreases the internal energy of the molecules. The fraction of higher-energy direct-loss products signal is considerably greater for the thermal sample because of its higher energy. However, the identity of the dissociation products is blurred by the thermal translational energy along the detection axis. If a single dissociation path is open and the TOF peaks are clearly distinct, the thermal data are preferable for making thermochemical determinations because we know the sample internal energy distribution is Boltzmann-like. However, when several dissociation channels are open or mass peaks overlap with each other, the thermal data are unusable and the molecular beam data are then used instead. The TOF spectra obtained with the molecular beam consist of signal from the molecular beam and signal from background gas in the chamber. The latter can be easily distinguished from the molecular beam signal by the much broader peak width of the parent ion [16, 17]. The molecular beam data were thus corrected for the ~20% thermal background signal by subtracting scaled thermal TOF spectra from the beam spectra.

Results

The threshold photoelectron (TPE) spectra obtained for thermal samples of the three compounds are shown together in Figure 2. For each molecule, the adiabatic ionization energy (IE) is measured from the onset of threshold electron signal. These IE measurements are difficult to interpret because the onsets are very indistinct. Similarly weak onsets have been found previously in photoelectron and absorption spectra [3, 18–20]. The poorly defined onsets for these compounds can be explained in terms of small Franck–Condon overlaps between the ion and neutral ground state geometries. As discussed in the following section, the minimum-energy structures of the neutrals and molecular ions are very different. Thus, there is a large (~1 eV) shift between the adiabatic and vertical ionization energies. Individual IE values are given in each of the following sections dealing with the particular compounds. They are also listed, along with the derived thermochemistry from this work, in Table 1.

Tetraethylsilane, (Et)$_4$Si

In a previous study [2], an adiabatic ionization energy of 9.03 ± 0.03 eV was reported. The 0 K onset for the ethyl loss reaction (the only dissociation path found in this energy range) was determined to be 9.85 ± 0.05 eV. Only one dissociation path was found, giving ethyl radical and the triethylsilylium (Et_3Si^+) fragment ion. Using the Pedley and Rylance [21] value for the tetraethylsilane heat of formation, we arrive at a $\Delta_f H°$ (0 K) for the molecular ion of 660 ± 15 kJ mol^{-1}. By assuming no reverse activation barrier for the direct loss reaction, a 0 K activation energy of 0.82 ± 0.05 eV was found, leading to a $\Delta_f H°$ (0 K) value of 609 ± 16 kJ mol^{-1} for the triethylsilylium ion (Table 2).

Triethylsilane, (Et)$_3$SiH

The adiabatic IE of this compound was measured to be 9.26 ± 0.03 eV. For this molecular ion, most of the signal comes from ethane loss over the photon energy range 10.0–10.9 eV; in fact, it is the only dissociation channel from 9.5 to 10.5 eV (see Figure 3).

The TOF distribution for the ethane loss fragment, $C_4H_{10}Si^{+\cdot}$, is asymmetrically broadened toward the higher times of flight, which means that this reaction is slow. Under these circumstances, it is best to extract the dissociation onset by measuring the dissociation rate as a function of the ion internal energy and to model these rate constants with the statistical RRKM theory. The two parameters needed to model the rate constant are the dissociation energy E_0 and the activation entropy. The latter is derived from the assumed vibrational frequencies of the transition state and the vibrational frequencies of the molecular ion which are known from ab initio MO calculations. This procedure is similar to that employed in the analysis of the tetraethylsilane data [2]. Near the dissociation threshold, the C_2H_6 loss rate constant curve matches an RRKM calculation with an activation entropy of −4 J K^{-1} mol^{-1}. The corresponding 0 K activation energy of 0.69 ± 0.03 eV gives a 0 K appearance energy (AE) of 9.95 ± 0.03 eV. As discussed in more detail in the ab initio molecular

Table 1. Ethylsilane (Et_nSiH_{n-4}) neutral and ion thermochemistry[a]

Compound	$\Delta_f H°$ (298 K)/kJ mol^{-1} Experiment	Calculation	IE_{adiab}/eV	$\Delta_f H°$ (ion, 298 K)/kJ mol^{-1} [f,g]
Tetraethylsilane	−265.4 ± 15.3[b]	−271.5[c]	9.03 ± 0.03[d]	606 ± 15[d]
(Et_4Si)	−297.0 ± 5[c]	−268.0[f]	8.9[g]	
	−237.4[g]	−300.8[h]		
	−238 ± 18.8[i]			
Triethylsilane	−200.9 ± 15.2[b]	−190.7[c]	9.26 ± 0.03[d]	693 ± 16[d]
(Et_3SiH)	−217 ± 5[e]	−197.2[f]	9.5[g]	
	−165.3[g]	−214.2[h]		
	−151.5 ± 10.5[k]	−203.8[i]		
	−205.7 ± 20[d]	−195.5[d,l]		
Diethylsilane	−182.5 ± 5.8[b]	−110.8[c]	9.70 ± 0.03[d]	794 ± 21[d]
(Et_2SiH_2)	−98.3[g]	−115.5[f]	9.8[g]	
	−141.5 ± 21[d]	−129.5[j]		
		−128.9[h]		
		−122.7[d,l]		

[a]298 K values can be converted to 0 K values for Et_nSiH_{n-4} by adding 35.6, 46.2, and 34.0 kJ/mol for n = 4, 3, and 2, respectively. These values have been calculated using the ab initio MO calculated vibrational frequencies for these molecules and ions.
[b]Pedley and Rylance [21].
[c]Frierson et al. [22].
[d]This work.
[e]Voronkov et al. [23].
[f]Chen and Allinger [24].
[g]Potzinger et al. [3].
[h]Group additivity and ab initio MO results of Gordon et al. [25].
[i]Iseard et al. [26].
[j]Ethyl group additivity calculations of O'Neal and Ring [27], based on Pedley and Rylance [21].
[k]Tel'noi et al. [28].
[l]Ab initio MO result with isodesmic reaction (this work) and the triethylsilane $\Delta_f H°$ from Pedley and Rylance [21].

orbital section, we suggest that this product ion may have the "silene" structure shown in Figure 4D.

At higher energies, we observe both H· atom and ethyl radical loss products from the triethylsilane ion. The H· atom loss channel is particularly interesting because it yields the triethylsilyl ion, the same product obtained in the ethyl loss from tetraethylsilane [2]. In order to distinguish these ions from parent ions and from the ethane loss product, it is necessary to analyze the molecular beam data that provide the necessary mass resolution. The onsets for these higher energy channels cannot be obtained simply from an appearance energy because the rate constants near their threshold will be much smaller than the lower energy ethane loss reaction. Thus, the onsets are shifted to higher energy by the so-called competitive kinetic shift [32, 33]. An observable amount of signal for the higher energy products is found only at the point at which their rate constants reach at least a few percent of the

Table 2. Fragment neutral and ion heats of formation[a]

Species	$\Delta_f H°$ (298 K)/kJ mol^{-1}	$\Delta_f H°$ (0 K)/kJ mol^{-1}
$\cdot C_2H_5$	120[b,c]	132
C_2H_6	−84.0[d]	−68.4
$\cdot H$	217.99[d]	216.035[d]
Et_3Si^+	567 ± 16[e]	609 ± 16[e]
Et_2SiH^+	657 ± 16[e]	688 ± 16[e]
$EtSiH_2^+$	761 ± 16[e]	781 ± 16[e]
$C_4H_{10}Si^{+\cdot}$	845 ± 20[e]	878 ± 20[e]
$C_2H_6Si^{+\cdot}$	931 ± 20[e]	≤951 ± 20[e]

[a]298 and 0 K values are converted using vibrational frequencies calculated by ab initio MO methods.
[b]Seakins et al. [29].
[c]Cao and Back [30].
[d]Lias et al. [31].
[e]This work.

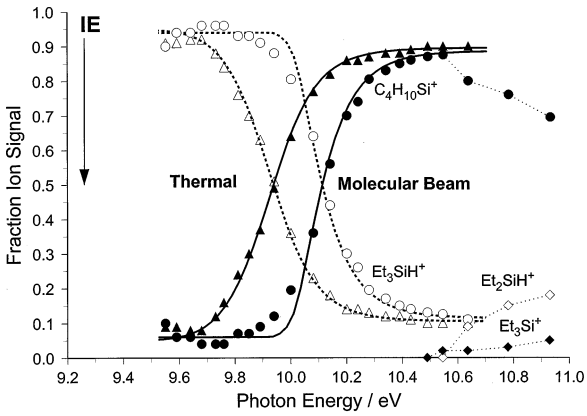

Figure 3. Breakdown diagram for triethylsilane. The open symbols are for the parent ion, whereas the solid symbols are for the daughter ions. The triangles are the thermal data, whereas the circles are for the molecular beam data. The fit given for the C_2H_6 loss reaction is obtained through explicit consideration of the energy distribution and rate constant function, as was done for tetraethylsilane. In this case, the effective internal temperature of the molecular beam sample was near 158 K. Where other reactions begin to appear, lines are drawn between data points and no simulation is given. However, these higher energy points allow the estimation of rate constant values used for the thermochemical measurement, as described in the text.

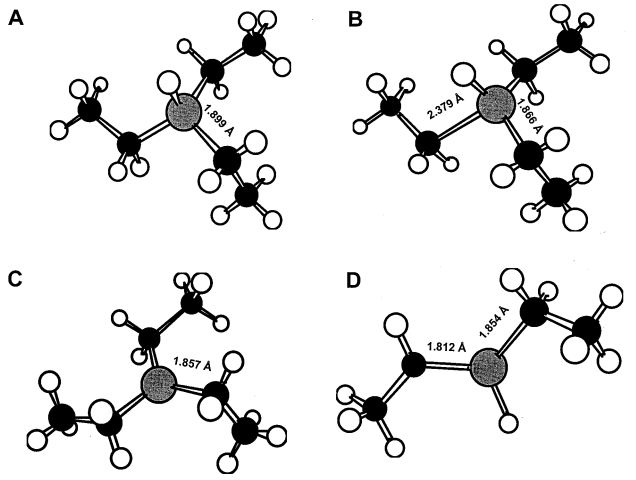

Figure 4. Ab initio molecular orbital minimum energy structures at the UHF/6–31g* level: (**A**) triethylsilane, (**B**) triethylsilane ion, (**C**) triethylsilylium cation, (**D**) 3-sila-2-pentene ion ($C_4H_{10}Si^{+\cdot}$) formed by β-elimination of C_2H_6 from B.

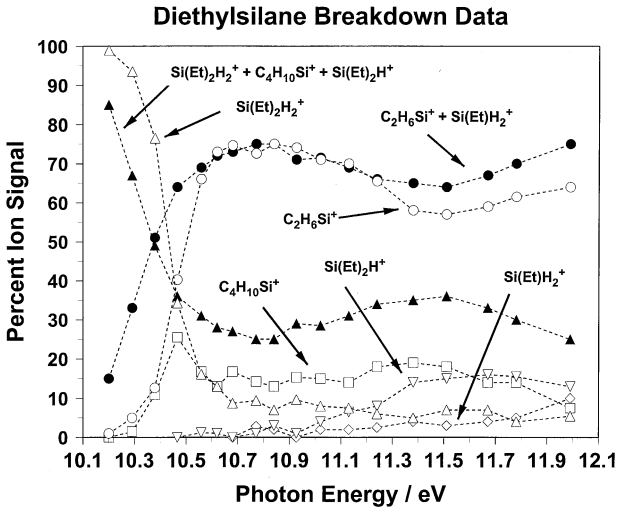

Figure 5. Breakdown data for diethylsilane. Lines are drawn between the points (no simulation was performed). Solid symbols are used for thermal data (for which mass resolution was inadequate to distinguish ions which differ by only 2 mass units), whereas open symbols are used to signify molecular beam data.

ethane loss rate constant. To model these higher energy reactions, we turn again to the rate analysis with RRKM fitting to extract the E_0. However, at these energies, the total rate constant [$k_{tot} = k(H)+k(C_2H_5)+k(C_2H_6)$] is already too fast to be measurable. Thus, we are forced to analyze the TOF data in terms of ratios of rate constants that are related to the ratio of ion signals (TOF peak areas):

$$\frac{k_1}{k_2} = \frac{\text{Area}_1}{\text{Area}_2} \tag{2}$$

The RRKM analysis of this ratio allows us to determine the shift in the onset energy between the $H^{\cdot}$ and ethyl loss reactions. The ethyl loss reaction is thus found to have an E_0 that is 0.073 eV below the $H^{\cdot}$ loss reaction onset. This difference is largely independent of the assumed activation energy and entropy.

In addition, the absolute E_0 values can be estimated by considering this competitive shift explicitly. By modeling the ethane loss reaction with an RRKM curve with a low $\Delta S^{\ddagger}$ (-4 J mol^{-1} K^{-1}) and the direct ($H^{\cdot}$ and $C_2H_5^{\cdot}$) loss reactions with two extremes of -6 and $+36$ J mol^{-1} K^{-1}, we obtain a range of activation energies that are consistent with the breakdown diagram of Figure 3. In this manner, we find that E_0 for the H loss reaction lies between 0.82 and 1.05 eV. This E_0 estimate of 0.94 ± 0.12 eV and the ethyl loss E_0 of 0.87 ± 0.12 eV help us to identify the neutral thermochemistry, as discussed below.

Diethylsilane, $(Et)_2SiH_2$

The adiabatic IE of this compound was found from TPES to be 9.70 ± 0.03 eV, which is 0.1 eV lower than the PES value of Potzinger et al. [3] value (see Table 1). The dissociation behavior for diethylsilane is unfortunately complicated by the fact that both ethane and hydrogen molecule are lost at the lowest energies (see Figure 5). Although the product ion structures are uncertain, the ab initio calculations suggest a silene product ion structure (see that section for details). Because we cannot distinguish H_2 loss product from parent ion in the thermal spectra, we use the higher mass resolution of the molecular beam data to make thermodynamic determinations. Although we cannot precisely measure the degree of cooling in the free expansion, we can estimate an average internal energy of 74 meV for the molecular beam sample of diethylsilane from the breakdown data, as explained in the experimental section. This corresponds to an effective Boltzmann temperature of ~183 K. The hydrogen and ethane molecule loss threshold energies are apparently within 0.1 eV of each other, so it is impossible to say with much certainty what the individual rate constants are. We thus estimate the onset from this breakdown diagram. In order to take into account the kinetic shift expected for these rearrangement reactions, we use the same ~0.15 eV shift observed for ethane loss from triethylsilane ion. That is, the crossover point C_0 will be shifted from the 0 K threshold by:

$$C_0 = E_0 + k.s. - \langle E \rangle_{MB} \tag{3}$$

For the ethane loss reaction of triethylsilane, we had $C_0 - E_0 = 0.155$ eV and $\langle E \rangle_{MB} = 0.097$ eV, giving a kinetic shift of 0.252 eV. Using this kinetic shift value, a C_0 of 10.44 eV, and a $\langle E \rangle_{MB} = 0.078$ eV for the ethane/hydrogen loss reaction of diethylsilane gives a 0 K appearance energy of 10.26 eV. This corresponds to a 0 K activation energy of 0.56 ± 0.05 eV.

Although the ethane loss reaction dominated all of

Table 3. Neutral and ionic silane energies from ab initio MO calculations

Species	Structure	HF/6–31 g* energy/Hartrees	ZPVE[a]/kJ mol^{-1}	Relevant relative energy
Starting compounds	Et_4Si	−603.532460700	674.6	IE = 7.695 eV
	Et_4Si^+ (molecular ion)	−603.247606156	669.2	
	Et_3SiH	−525.45673140	527.1	IE = 7.993 eV
	$Et_3SiH^{+\cdot}$ (molecular ion)	−525.160899509	521.2	
	Et_2SiH_2	−447.380345403	379.4	IE = 8.350 eV
	$Et_2SiH_2\cdot$ (molecular ion)	−447.071334753	373.7	
Ethyl silylium ions	Et_3Si^+	−524.625957955	504.6	
	Et_2SiH^+	−446.532263296	355.6	
	$EtSiH_2^+$	−368.433170909	207.2	
$C_4H_{10}Si^{+\cdot}$ ions	$Et_2Si^{+\cdot}$ (α)	−445.916100124	332.7	24.7 kJ mol^{-1}
	$EtSi(=CHCH_3)^{+\cdot}$ (β)	−445.922581066	325.0	0
	$EtSi(-CH_2CH_2)H^{+\cdot}$ (γ)	−445.914351156	324.7	21.3 kJ mol^{-1}
	Silacyclopentane ion	−445.884741460	320.2	94.5 kJ mol^{-1}
$C_2H_6Si^{+\cdot}$ ions	$EtSiH^{+\cdot}$ (α)	−367.816166019	183.0	30.3 kJ mol^{-1}
	$CH_3CH{=}SiH_2^{+\cdot}$ (β)	−367.825276624	176.7	0
	$CH_2CH_2{-}SiH_2^{+\cdot}$ (γ)	−367.820578041	176.3	12.0 kJ mol^{-1}
Silane	SiH_4	−291.225134321	80.3	

[a]Corrected zero-point vibrational energy.

the TOF data for diethylsilane for photon energies between 10.0 and 10.9 eV, at higher energies, we observed the appearance of the H$^\cdot$ atom and ethyl radical loss products. Again, the competitive rates of the various reactions prevent accurate determination of the threshold energy. However, we can estimate the shift in onset energy ΔAE by RRKM simulation of the relative signals. This leads to a shift of 0.079 eV (H is lost at lower energy).

The absolute E_0 values can again be estimated by using a range of $\Delta S^\ddagger$ values for the H loss reaction. This yields a range of 0.64–0.92 eV. Thus, we find E_0 values for H$^\cdot$ and $C_2H_5^\cdot$ loss of 0.78 ± 0.14 eV and 0.86 ± 0.14 eV, respectively.

Ab Initio Molecular Orbital Calculations

The energetics, geometry, and vibrational structure of many of the important species in the ion dissociations were explored using ab initio molecular orbital methods. We used the Gaussian [34] set of programs, run on a Convex 3840 at UNC or Cray T916 at the North Carolina Supercomputer Center. Geometry optimizations and frequency calculations were performed at the HF/6–31 g* level. Frequency correction factors used (0.8929 for individual frequencies, 0.9135 for zero-point vibrational energies) are those recommended by Pople et al. [35].

Typical single Si–C bond lengths in neutral molecules are about 1.9 Å. However, upon ionization of the ethyl silanes, one of the Si–C bond lengths increased to 2.30–2.38 Å, whereas the others contracted to 1.86–1.87 Å. This "loose ion-radical complex" structure is similar to one reported by Vekey et al. [36] for the dimethylethylsilane ion. This extended Si–C bond is responsible for a Franck–Condon shift between adiabatic and vertical ionization energies of ~1 eV for these compounds.

The neutral and ion calculations also allowed a comparison between experimental and predicted adiabatic ionization energies (Table 3). Using the electronic and vibrational zero-point energies, we predict IE values of 7.695, 7.993, and 8.350 eV for the tetra-, tri-, and diethylsilane species. These values underestimate the experimental result by a constant 1.32 eV (~15%). The fact that the deviation is constant to some extent validates the experimental determinations, although the shift itself is likely to result from the relatively low level of theory used in the calculations. We have found a similar discrepancy between calculated and measured IEs for the case of 2-bromobutane [37].

The closed-shell trivalent structures (ethyl silylium cations) found for the direct loss reactions appear to be quite tightly bound, with Si–C bond lengths of 1.84–1.86 Å. These structures are planar at the Si ion center. An example of this structure is the triethyl silylium cation shown in Figure 4C.

The major ion produced in the Et_3SiH photoionization is the open shell $C_4H_{10}Si^+$ ion which results from the loss of ethane. It is also produced as a minor product via H_2 loss from diethylsilane ion. The origin of the H atom that the ethyl group picks up may be expected to determine both the reaction mechanism (type of elimination: α, β, γ) and the product ion structure. If this H is originally attached to the silicon, it is an α elimination. This produces a λ^2-silaniumyl structure, which has both the charge and the unpaired electron localized at the silicon atom with λ^2 signifying that silicon has a coordination number of 2, according to IUPAC nomenclature rules. If the H comes from the methylene ($-CH_2-$) or α carbon of one of the ethyl groups, the reaction is 1,2 or β elimination. This leaves a partial double bond between carbon and silicon of length 1.81 Å (see Figure 4D), with the free electron spending most of its time near the α carbon. This

structure would be a silene, with a C=Si bond. If the H atom comes from one of the methyl groups, we have a 1,3 or γ elimination reaction. This leaves the radical site at the terminal carbon, forming a C_2H_4 ligand that may be bound to silicon at either or both carbons, possibly forming a silacyclopropane. As listed in Table 3, the energies of these $C_4H_{10}Si^+$ structures are quite similar. The β-elimination product is the lowest in energy, but only by about 20 kJ mol^{-1}. Finally, we calculated the silacyclopentane ion structure, which can result from at least two H transfers. However, it was found to be nearly 100 kJ mol^{-1} higher in energy than the other isomers. It should be pointed out that it is the activation energy, not the reaction energy, which largely determines which structure will be formed. Nevertheless, some experimental evidence for the formation of the lower-energy silene structures is given by Gusel'nikov et al. [38].

In similar fashion, the α, β, and γ elimination structures were calculated for the $C_2H_6Si^{+\cdot}$ case (H_2 loss of diethylsilane ion), for which the nonparticipating ethyl group of the similar $C_4H_{10}Si^{+\cdot}$ ion is simply replaced by H˙. Again, the β-elimination product was found to be lowest in energy (see Table 3), but now only by 12 kJ mol^{-1}. Thus the γ elimination product may also participate in the H_2 loss reaction of diethylsilane ion.

A final theoretical determination was made using isodesmic reactions to estimate the ethyl group value for the neutral molecules:

$$4Et_3SiH \rightarrow 3Et_4Si + SiH_4 \quad (4)$$

$$3Et_2SiH_2 \rightarrow 2Et_3SiH + SiH_4 \quad (5)$$

The calculated 0 K enthalpies of these reactions were determined at the HF/6–31 g* level to be 7.7 and 2.6 kJ mol^{-1}, respectively. By using the experimental heats of formation for Et_4SiH [21] and SiH_4 [31], it was possible to determine the 0 K $\Delta_fH°$ values for Et_3SiH and Et_2SiH_2. Equation 4 yielded a $\Delta_fH°$ (0 K) of −149.3 kJ mol^{-1} for triethylsilane. This corresponds to an ethyl group value ($\Delta\Delta_fH°$) of 69.9 kJ mol^{-1} at 298 K. Similarly, we used eq 5 and the Pedley and Rylance $\Delta_fH°$ value for triethylsilane. This gave a $\Delta_fH°$ (0 K) for diethylsilane of −88.7 kJ mol^{-1} (−122.7 kJ mol^{-1} at 298 K), which is some 60 kJ/mol higher than that reported by Pedley and Rylance [21]. However, the ethyl group value of 78.2 kJ mol^{-1} associated with eq 5 is fairly close to the 69.9 kJ mol^{-1} value found for eq 4. Although starting with other Et_4Si $\Delta_fH°$ values (such as given in [23]) changes the derived group value, the differences are less than 10 kJ mol^{-1}. From these results we conclude that the Pedley and Rylance value for the heat of formation of diethyl silane is too high by about 60 kJ mol^{-1}, and that the additivity schemes currently in the literature [22, 25, 27, 39] suggest ethyl group values to silanes that are too high (see Table 4).

Table 4. Comparison of ethyl group values in neutral and ionic silanes (kJ/mol at 298K)

Reaction	Neutral molecules			Molecular ions	
$Et_4Si \rightarrow Et_3SiH$	60[a]	64.5[b]	87[c]	87[a]	145[d]
$Et_3SiH \rightarrow Et_2SiH_2$	59[a]	18.4[b]	85[c]	101[a]	115[d]

[a]This work.
[b]Pedley and Rylance [21].
[c]Gordon et al. [39] and Walsh [41] based on data of Voronkov [23].
[d]Luo et al. [43] based on data of Potzinger et al. [3] and Walsh [41].

Implications for Neutral and Ionic Thermochemistry

The determination of ion heats of formation depends upon the reliability of values for the neutral precursors. There is considerable debate over which experimental values (in Table 1) should be used [3, 21, 23, 26, 28] because the bomb calorimetry determinations are subject to incomplete combustion. Additivity rules and low-level theory (MMX, AM1, MNDO) have been matched to various experimental data sets, with limited success because they depend to some extent on the experimental values chosen [22, 40–43]. From even a brief review of the experimental literature, the internal inconsistency of the ethylsilane heats of formation is quite clear [24].

In the discussion of derived thermochemistry, we take advantage of the well-established neutral fragment heats of formation given in Table 2 and the scheme presented in Figure 6. For the ethylsilanes, we start from the value for tetraethylsilane reported by Pedley and Rylance [21]. As reported in the previous work, our Et_4Si IE of 9.03 ± 0.03 thus gives a 0 K $\Delta_fH°$ for the tetraethylsilane ion of 659.5 ± 15 kJ mol^{-1}. Subsequently, the ethyl-loss activation energy of 0.82 ± 0.05

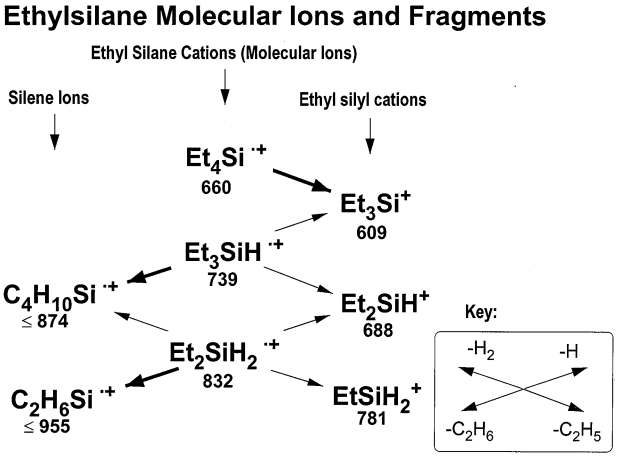

Figure 6. Spaghetti diagram showing linkages of fragment ions and experimental 0 K heats of formation in kJ mol^{-1}. The silene product ion heats of formation given are upper limits, as indicated in the text.

eV derived in that study leads to a 0 K $\Delta_f H°$ for Et_3Si^+ of 608.6 ± 16 kJ mol^{-1}.

The H loss reaction of triethylsilane is expected to produce the same triethylsilylium ion fragment. The 0 K AE for this reaction of 10.20 ± 0.12 eV thus leads to an estimate of the triethylsilane neutral 0 K heat of formation of −159.5 ± 20 kJ mol^{-1}. This agrees very well with the Pedley and Rylance [21] value of −154.7 ± 15 kJ mol^{-1}, so we accept this literature value. Doing so leads to a 0 K $\Delta_f H°$ of the triethylsilane molecular ion of 738.8 ± 16 kJ mol^{-1}. The ΔAE (H,Et) value of −0.073 ± 0.01 eV for triethylsilane further implies a 0 K $\Delta_f H°$ for Et_2SiH^+ of 687.6 ± 16 kJ mol^{-1}. Because the ethane elimination involves a tight transition state, the ethane loss of E_0 for triethylsilane of 0.69 ± 0.03 eV is the energy of the transition state, and thus gives only an upper limit of 873.7 ± 16 kJ mol^{-1} for the 0 K $\Delta_f H°$ for $C_4H_{10}Si^+$.

Because the Et_2SiH^+ ion is also produced from the diethylsilane ion, the H-loss appearance energy of 10.48 ± 0.14 eV for diethylsilane implies a neutral diethylsilane 0 K $\Delta_f H°$ of −107.5 ± 21 kJ mol^{-1}, or a 298 K value of −141.5 kJ mol^{-1}. Although some theoretical estimates fall within this range, in the absence of other reliable experimental values, we recommend our own. This gives a 0 K $\Delta_f H°$ for the diethylsilane molecular ion of 828.4 ± 21 kJ mol^{-1}.

The heat of formation of diethylsilane of −141.5 kJ mol^{-1} is more than 40 kJ mol^{-1} above that reported by Pedley and Rylance [21], and more than 40 kJ mol^{-1} below that of Voronkov et al. [23]. Although our value for the diethylsilane heat of formation does not have a great deal of precision because of the error in determining the dissociation onset of H$^\cdot$ loss, it is difficult to imagine that it could be outside of the stated error limits. In support of this, we point to our ab initio molecular orbital calculation that suggests that this 298 K $\Delta_f H°$ is even higher (−123 kJ mol^{-1}).

The 0 K activation energy for loss of H_2 and C_2H_6 from diethylsilane ions of 0.56 ± 0.05 eV obtained in this work suggests an upper limit for the 0 K $\Delta_f H°$ values of 882.4 ± 21 and 950.8 ± 21 kJ mol^{-1} for $C_4H_{10}Si^{+\cdot}$ and $C_2H_6Si^{+\cdot}$, respectively. The difference of 8.7 kJ mol^{-1} between this $C_4H_{10}Si^{+\cdot}$ value and that obtained from triethylsilane falls within the reported error limits (due to uncertainty in the neutral $\Delta_f H°$ for diethylsilane), but can also be attributed to differences in reverse activation energy for the H_2 and C_2H_6 loss reactions. The ΔAE (H,Et) value of 0.079 ± 0.01 eV for diethylsilane suggests a 0 K $\Delta_f H°$ for $EtSiH_2^+$ of 781.3 ± 16 kJ mol^{-1}.

These results provide new estimates of ethyl group values for the neutral molecules and various ion species at 298 K. For the neutral molecules, we find ethyl group values of 59.7 and 59.4 kJ mol^{-1} for the shift from tetraethylsilane to triethylsilane and from triethylsilane to diethylsilane, respectively (see Table 4). Our isodesmic calculation finds values of 62.5 and 66 kJ mol^{-1}. Both of these values are considerably lower than those claimed by Voronkov [23] and by Walsh [41].

It is evident from Table 4 that the molecular ion (298 K) ethyl group values are larger than those for the corresponding neutral molecules. We find values of 87 and 101 kJ mol^{-1} which come directly from the ΔAE measurements. Our derived ethyl group values for the ions are much lower than those reported previously by Luo et al. [43] (see Table 4). This discrepancy is a result of the larger ethyl group values used for the neutral ethyl silanes by Luo et al. [43]. The 298 K ethyl loss activation energies were found to be a rather constant 92 ± 10 kJ mol^{-1} for all three molecular ions. This results in ethyl group values for the ethylsilylium ions that are roughly the same as for the molecular ions. For the silene ions, the ethyl group value appears as the difference between our two upper limit estimates to be 81 ± 10 kJ mol^{-1}.

The $Et_2Si{=}CHCH_3^{+\cdot}$ ion reported by Gusel'nikov et al. [38] is not observed in our experiments and thus has a 0 K TS $\Delta_f H°$ of at least 840 kJ mol^{-1}. This is in agreement with the $\Delta_f H°$ value reported by that group of roughly 885 kJ mol^{-1}.

Summary

The "spaghetti diagram" in Figure 6 illustrates the possible connectivity of the three experiments. In three cases, two different molecular ions dissociate to produce the same mass fragment ion. The formation of the ethylsilylium (trivalent silicon) cations is always assumed to occur by simple bond cleavage. Thus, no appreciable error is introduced by taking the activation energy to be the reaction energy. In going from the larger to smaller precursors, the reactions become more complex, so the thermochemistry is built upon the simpler tetraethylsilane ion results of the previous work. By assuming the same heat of formation for these common fragment ions, we have been able to hook-and-ladder our way to determining the energies of all of the product ions. Triethylsilane and diethylsilane ions dissociate to form radical ions that may be silenes, although their structures are uncertain. The lowest energy structure, found by ab initio molecular orbital calculation, is the β-elimination structure with partial Si–C double bonding. However, the α and γ elimination structures lie within 30 kJ mol^{-1} and cannot be ruled out. Because these products are formed by rearrangement (i.e., H$^\cdot$ transfer), the measured activation energies are only upper limits to the product energy. We can form a complete picture using our recommended neutral heats of formation and IE, AE, and ΔAE values.

Ethyl group values for the neutral and ionic species have been obtained which corroborate some of the previous work, but exclude others. The ionization and dissociation thresholds have been measured with good accuracy.

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